

Oxygen Vacancy Induced Ferromagnetism in V_2O_{5-x}

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Ab initio calculations within density functional theory with generalized gradient approximation have been performed to study the effects of oxygen vacancies on the electronic structure and magnetism in undoped V_2O_{5-x} ($0 < x < 0.5$). It is found that the introduction of oxygen vacancies would induce ferromagnetism in V_2O_{5-x} with the magnetization being proportional to the O vacancy concentration x . The calculated electronic structure reveals that the valence electrons released by the introduction of oxygen vacancies would occupy mainly the neighboring V d_{xy} -dominant band which then becomes spin-polarized due to intra-atomic exchange interaction, thereby giving rise to the half-metallic ferromagnetism.

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Ferromagnetism in diluted magnetic semiconductors (DMSs) has recently received a lot of attention for fundamental research and possible applications in spintronics[1, 2, 3]. Although a number of transition-metal (TM) oxide based DMSs, such as Co:TiO₂ and Co:ZnO, have been reported,[4, 5] the origin of ferromagnetism in many cases is still under much debate.[6, 7, 8] The controversy of the magnetic origin lies in the structure of DMSs in the first place, i.e., whether it is due to the intrinsic contribution from the DMS phase or from some secondary phases.[4] It is noticed that even if the formation of the secondary phases could be ruled out, the valence effect on ferromagnetism, the role of the microscopic complex structure formed by oxygen, dopant, and host TM elements need to be clarified. Oxygen vacancies may also play an important role for the ferromagnetism in oxide based DMSs because oxygen vacancies not only modulate the valence of neighboring TM elements but also cause a change of the band structure of host oxides; both factors in turn can make significant contribution to the ferromagnetism.[9] Several conflicting experimental results of oxide based DMSs could be partly related to the difference in their oxygen vacancies because of distinct sample growth conditions.[4, 9]. Therefore, understanding of the role of oxygen vacancies in TM oxides is essential to clarify the origin of the ferromagnetism in the oxide based DMSs.

Vanadium oxides consist of compounds with single [V_2O_5 (V^{+5}), V_2O_4 (V^{+4}), V_2O_3 (V^{+3}) and VO (V^{+2})] and mixed valences which form a fascinating class of multifunctional materials. Vanadium oxides have been

widely used in catalytic, optical, electrical and electrochemical devices.[10, 11, 12] V_2O_5 is a diamagnetic insulator at room temperature with an orthorhombic layered structure. It undergoes a phase transformation to a metallic phase at about 530 K.[13, 14] By comparison, V_2O_4 is a diamagnetic semiconductor with a tetragonal rutile structure below a critical temperature of ~ 340 K and a metal with a monoclinic structure above.[15]. While the physical properties for various vanadium oxides have been extensively studied,[16, 17, 18] the role of oxygen vacancies on the structural, electronic and magnetic properties of V_2O_5 remains yet to be explored. We have therefore performed *ab initio* theoretical studies of the electronic structure and magnetism in V_2O_{5-x} . Our calculations reveal that the presence of oxygen vacancies introduces electrons onto the neighboring V d_{xy} dominant conduction band which is then spin splitted due to intraatomic exchange interaction, leading to the formation of the magnetic order. Our finding calls for critical re-examinations of the role of the intrinsic O vacancies in the formation of magnetism in TM based DMSs, and also suggests a new direction for search for ferromagnetism in semiconductors.

Our *ab initio* calculations are based on density functional theory with the generalized gradient approximation to the electron exchange-correlation interaction.[19]. Two approaches are used to model the oxygen vacancies in V_2O_{5-x} . One is the so-called virtual crystal approximation (VCA). In V_2O_{5-x} , x O atoms are removed, and this is equivalent to increase the number of the conduction electrons by $2x$. In the VCA, this is simulated by artificially increasing the electron and atomic number of V from 23.0 to $23.0 + x$, i.e., replacing the V atoms by the virtual atoms with an atomic number of $23.0 + x$. We have performed self-consistent band struc-

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FIG. 1: (Color) Isosurface of the spin density of V_2O_{5-x} ($x = 0.125$) in the $1 \times 2 \times 2$ supercell. The numbers are the numberings of the V atoms in the unit cell that are referred to in the text and Table I.

ture calculations for V_2O_{5-x} with several x values in both nonmagnetic (NM) and ferromagnetic (FM) states. We use the highly accurate full-potential linearized augmented plane wave (FLAPW) method, as implemented in WIEN2k package.[20] The experimental lattice constants used here are $a = 11.512$ Å, $b = 3.564$ Å, and $c = 4.368$ Å. [21] The cutoff angular momentum for the spherical harmonics expansion is 10 and as many as ~ 120 augmented plane waves per atom are included.

The other approach is the supercell (SC) method which is much more CPU time-consuming especially for small x values. Nonetheless, the SC method is more realistic. In particular, we can study local structural, electronic and magnetic properties in the vicinity of the O vacancies. We have carried the SC calculations for the $x = 0.25$ and 0.125 cases using the $1 \times 1 \times 2$ and $1 \times 2 \times 2$ supercells, respectively. Pure V_2O_5 has a layered structure with two formula units (f.u.) per unit cell.[21] Each layer contains edge- and corner-shared VO_5 pyramids with three types of O atoms, namely, apical oxygen (O1), chain oxygen (O2) and bridge oxygen (O3), as illustrated in Fig. 1. In order to investigate which kind of the O vacancies is energetically favorable, we perform *ab initio* structural optimizations using the $1 \times 1 \times 2$ supercell with one O1 or O2 or O3 vacancy, respectively. We use the computationally more efficient projector augmented wave (PAW) method,[22] as implemented in VASP package.[23] A large cutoff energy of 400 eV is used, and the equilibrium atomic positions are obtained when the forces acting on all the atoms were less than 0.02 eV/Å. Our $1 \times 1 \times 2$ SC calculations show that the total energy per vacancy for the O1 vacancy is 1.41 and 2.15 eV lower than that of the O2 and O3 vacancies, respectively, suggesting that apical oxygen (O1) is the preferred O vacancy site. Thus, we perform the structural optimization for the $1 \times 2 \times 2$ SC with only the O1 vacancy. Our $1 \times 1 \times 2$ and $1 \times 2 \times 2$ SC calculations show that the O1 vacancy in the FM state has a lower total energy than in the NM state, respectively, by 78 and 86 meV per vacancy, showing that the ferromagnetism is stable in V_2O_{5-x} . The stable FM state is also found in the VCA calculations for all the x values considered. We also perform the self-consistent spin polarized calculations for the antiferromagnetic (AF) configuration with the initial magnetic moment on the V atom next to the vacancy being antiparallel to the other V atoms. However, the self-consistent calculations always converge to the FM state, indicating that the AF state is unstable.

Final self-consistent band structures for the $1 \times 2 \times 2$ supercell with the theoretically determined atomic structure were calculated using the FLAPW method. The

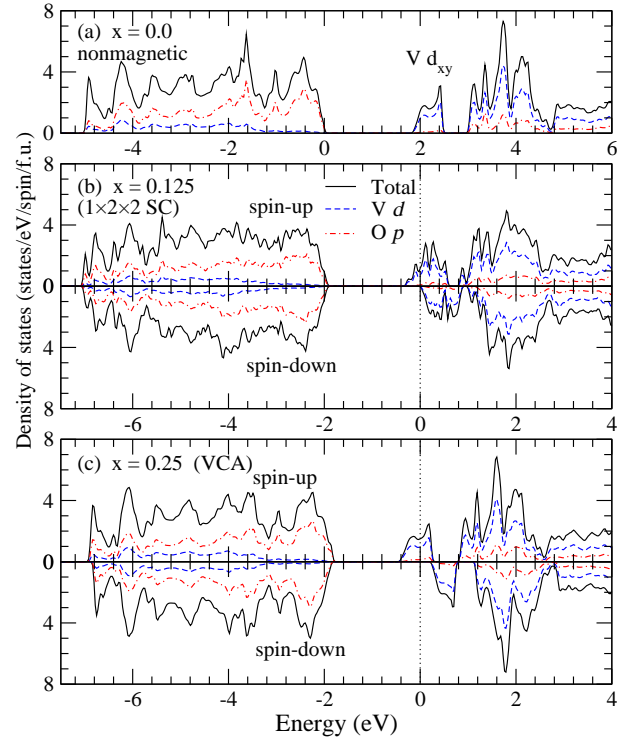


FIG. 2: Total and site-decomposed density of states for V_2O_{5-x} with (a) $x = 0.0$, (b) $x = 0.125$ (SC calculation) and (c) $x = 0.25$ (VCA calculation).

calculated V local magnetic moments for $x = 0.125$ are listed in Table I. The total magnetic moment is $2.0 \mu_B$ per vacancy, and is the same as that obtained from the VCA calculations. Majority of the magnetization is located on the V atoms (d_{xy} -orbital) next to the O vacancy (V7,V3,V9 in Fig.1) and also in the surrounding interstitial region, as can also be seen from Fig. 1 which shows the spin density distribution. The induced magnetization on all the O atoms are negative (i.e., antiparallel to that on the V atoms) and the sum of the O atomic moments is $-0.360 \mu_B$ per supercell. However, the local magnetic moments on *most* O atoms are negligible ($< 0.01 \mu_B$), though six O atoms have a magnetic moment of $0.01 \sim 0.05 \mu_B$.

Fig. 2(a) shows that pure V_2O_5 is a semiconductor with a band gap of ~ 1.8 eV. While the valence band is clearly O p dominant, the lowest conduction band is of mainly V d_{xy} character. Interestingly, Fig. 2(b) shows that when one O vacancy is introduced, the lowest conduction band is strongly spin-polarized, and the spin up one is partially occupied whilst the spin down one is still empty, resulting in a FM state with a spin moment of $2 \mu_B$ per vacancy. Clearly, when one O atom is removed, the two electrons released are added to the narrow V d_{xy} dominant conduction band. However, because of the rather strong V intra-atomic exchange interaction (I_{ex}) of ~ 0.354 eV,[24] this partially occupied V d band be-

TABLE I: Local magnetic moments (m_s) (μ_B/atom) of V atoms in the ferromagnetic V_2O_{5-x} ($x = 0.125$) from the $1 \times 2 \times 2$ supercell calculation. The total magnetic moment is $2.0 \mu_B$ per O vacancy. The locations of various V atoms are indicated in Fig. 1. Int. denotes the magnetization in the interstitial region. Also listed are the V-site decomposed density of states at the Fermi level $N(E_F)$ (states/eV/atom) in the nonmagnetic V_2O_{5-x} .

V	m_s	$N(E_F)$	V	m_s	$N(E_F)$
1 ($\times 2$)	0.049	0.43	8	0.073	1.29
2 ($\times 2$)	0.046	0.72	9	0.267	1.36
3	0.278	3.47	10	0.118	0.57
4	0.075	1.15	11 ($\times 2$)	0.039	0.37
5	0.177	0.69	12 ($\times 2$)	0.030	0.49
6	0.087	0.46	int.	0.595	1.99
7	0.360	4.35			

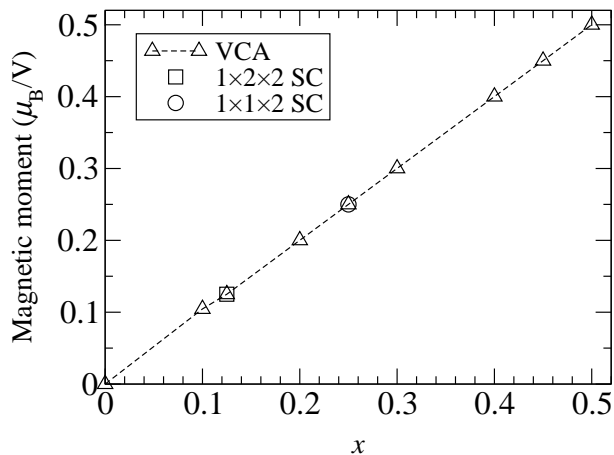


FIG. 3: Magnetic moment per V atom as a function of O vacancy concentration x from VCA and SC calculations.

comes magnetically unstable and spin split, giving rise to a ferromagnetic order, as the spin-polarized band structure for $x = 0.125$ and 0.25 in Fig. 2(b-c) shows. To

corroborate this Stoner mechanism for ferromagnetism, we also calculate total and site-decomposed density of states in the nonmagnetic V_2O_{5-x} ($x = 0.125$) in the $1 \times 2 \times 2$ supercell. Table I shows that V7 next to the O vacancy (see Fig. 1) has such a large local density of states at the Fermi level ($N(E_F)$) that the Stoner criterion ($I_{ex}N(E_F) > 1$) for the magnetization formation is satisfied. Fig. 3 shows the calculated magnetic moment per V atom as function of O vacancy concentration (x). Remarkably, the calculated magnetic moment per V atom are proportional to x . This is due to the fact that the additional $2x$ electrons released by removing x O vacancies go exclusively to occupy the lowest V d -conduction band of the majority spin, as mentioned above.

Summarizing, our *ab initio* calculations show that V_2O_{5-x} , with $0.0 < x < 0.5$ is ferromagnetic. The two valence electrons released by the introduction of each oxygen vacancy would occupy mostly the d_{xy} orbital of the V atoms next to the vacancy, and become fully spin-polarized due to intra-atomic exchange interaction, giving rise to the ferromagnetic order with a magnetic moment of $2\mu_B$ per vacancy. We note that recent experiments indicate possible room-temperature ferromagnetism in oxygen-deficient V_2O_{5-x} [25]. We also note that the recent *ab initio* calculations indicate the unexpected ferromagnetism observed in HfO_2 being also driven by intrinsic O vacancies.[26] Nevertheless, the microscopic mechanisms in the present and previous cases would be fundamentally different since in Ref. [26], the magnetic moment is centered at the O vacancy. Clearly, the present work calls for critical re-examinations of the magnetism in TM oxide based DMSs especially the role of the intrinsic O vacancies. The present work also suggests a new direction for search for ferromagnetism in semiconductors.

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